Limited effects of land use on soil dissolved organic matter chemistry as assessed by excitation–emission fluorescence spectroscopy and molecular weight fractionation

Roberts, Paula; Gibbons, James; Hill, Paul; Jones, David; Farrell, Mark

Soil Use and Management

DOI:
10.1111/sum.12295

Published: 01/12/2016

Peer reviewed version

Limited effects of land use on soil dissolved organic matter chemistry as assessed by excitation-emission fluorescence spectroscopy and molecular weight fractionation

PAULA ROBERTS[1], JAMES GIBBONS[1], PAUL W. HILL[1], DAVEY L. JONES[1], MARK FARRELL[2]

[1] *School of the Environment, Natural Resources and Geography, Bangor University, Bangor Gwynedd LL57 2UW, UK*

[2] *CSIRO Agriculture, PMB 2, Glen Osmond, SA, 5064, Australia*

Correspondence: P. Roberts p.roberts@bangor.ac.uk

50-char running head: Land use effects on soil OM chemistry is limited

Abstract

Dissolved organic matter (DOM) in soil solution represents a complex mixture of organic molecules and plays a central role in carbon and nitrogen cycling in plant-microbial-soil systems. We tested whether excitation-emission matrix (EEM) fluorescence spectroscopy can be used to characterise DOM in order to support previous findings that the majority of DOM is of high molecular weight (MW). EEM fluorescence spectroscopy was used in conjunction with MW fractionation to characterise DOM in soil solution from a grassland soil land management gradient in North Wales, UK. Data analysis suggested that three distinct fluorescence components could be separated and identified from the EEM data. These components were identified as being of humic-like or fulvic-like origin. Contrary to expectations, the majority of the fluorescence signal occurred in the low MW (< 1 kDa) fraction, although differences between soils from the differently managed grasslands were more apparent in higher MW fractions. We conclude that following further characterisation of the chemical composition of the fluorophores, EEM has potential as a sensitive technique for characterising the low MW phenolic fraction of DOM in soils.

Keywords: Dissolved organic matter, DOM, Size fractionation, Soil water, Ultrafiltration

Introduction

Dissolved organic matter (DOM) is a complex mixture of organic compounds which range in size from >100,000 to <100 Da (Farrell *et al*., 2011). Soil management and land use are recognised as key factors affecting DOM composition (Cookson *et al*., 2005). Excitation-emission matrix (EEM) fluorescence spectroscopy is an increasingly popular tool for characterisation of components of DOM in soils and sediments, with general attribution of fluorescence to high molecular weight (MW) compounds (McKnight *et al*., 2001; Chen *et al*., 2003; Santín *et al*., 2009). We investigated the EEMs of soils solutions from a catena sequence and management gradient of grassland soils. As DOM concentrations in soil solutions were highest in high MW fractions (>100 kDa; Farrell *et al*., 2011), we hypothesised that observed fluorescence would also be greatest in these high MW fractions.

Materials and methods

To test the effects of grassland management regimes on soil solution DOC chemistry, four replicate soil samples (0-15 cm depth) were collected from each of the five sites along a temperate agricultural grassland management, plant diversity and primary productivity gradient described by Farrell *et al.,* (2011). Management regimes are outlined in Table 1. A randomised block approach was used to reduce the potential error associated with using a single gradient (total n=20). Soil solution was extracted by centrifugal-drainage and MW fractionated by ultrafiltration (Farrell *et al*., 2011) resulting in 80 samples for EEM. Specific UV absorbance of soil solution DOC at 254 nm ($SUVA_{254}$) was used as an indicator of aromaticity (Fellman *et al*., 2009) and EEM spectra were obtained using methods described in Supplementary Information.

Results

There was a clear overall negative correlation between $SUVA_{254}$ and DOC concentration (r = -0.44; $p \leq 0.001$, n=80), indicating that as DOC concentrations increased, aromaticity of DOC decreased. Despite highest DOC concentrations in the largest (>100 kDa) fraction (Farrell *et al*. 2011), fluorescence was highest in the smallest MW fraction of all soils (<1 kDa; Fig. 1). The only exception to this was a large peak at 265/425 nm in the 10-100 kDa fraction of Soil 5. Parallel factor analysis (PARAFAC) best described three separate fluorescence components accounting for 98.9% of the variance in data (Table S2). Component 1 was dominated by the lowest MW fraction (Fig. 2) in all soils, with 84.3 ± 2.7% of component 1 found in the < 1 kDa fraction. Component 1 was present in fractions >100 kDa only in Soil 4. Component 2 was also dominated by the < 1 kDa fraction but significant amounts were present in the 1-10 kDa fractions of Soil 5. Distribution of components 1 and 2 between larger size fractions was soil-specific. Distribution of component 3 was variable with little difference between soil type or MW fraction. All three PARAFAC components have previously been attributed to humic-like or fulvic-like compounds often associated with large macromolecules (Table S2).

Discussion

Fluorescence was found in all MW fractions of the soils, but contrary to other studies of terrestrial dissolved organic matter (DOM) (Wang *et al*., 2011; Borisover *et al*., 2012; Nishimura *et al*., 2012), we found fluorescence to be dominated by low MW species. Soil management practices, plant diversity or above-ground net primary productivity (ANPP) had little effect on the fluorescence characteristics of these low MW fractions, and higher MW compounds appeared more sensitive to soil pedogenic features e.g. where localised waterlogging (e.g. soil 5) may alter rates and mechanisms of organic matter decomposition. As low MW compounds represent the most bioavailable DOM in soil and dominate C turnover (van Hees *et al*., 2005), our results suggest that EEMs may provide a simple diagnostic tool for

examining organic matter transformation and fractionation in soil solution (Bosco & Larrechi, 2008) but that further characterisation of the chemical composition of the fluorophores is required to fully understand the effects of land use on organic matter chemistry.

References

Borisover, M., Lordian, A. & Levy, G.J. 2012. Water-extractable soil organic matter characterization by chromophoric indicators: Effects of soil type and irrigation water quality. *Geoderma*, **179**, 28-37.

Bosco, M. & Larrechi, M.S. 2008. Rapid and quantitative evaluation of the effect of process variables on the kinetics of photocatalytic degradation of phenol using experimental design techniques and parallel factor (PARAFAC) analysis. *Annals of Bioanalytical Chemistry*, **390**, 1203-1207.

Chen, W., Westerhoff, P., Leenheer, J.A. & Booksh, K. 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental Science and Technology,* **37** 5701-5710.

Cookson, W.R., Abaye, D.A., Marschner, P., Murphy, D.V., Stockdale, E.A. & Goulding K.W.T. 2005. The contribution of soil organic matter fractions to carbon and nitrogen mineralization and microbial community size and structure. *Soil Biology and Biochemistry*, **37,** 1726–1737.

Farrell, M., Hill, P.W., Farrar, J., Bardgett, R.D. & Jones, D.L. 2011. Seasonal variation in soluble soil carbon and nitrogen across a grassland productivity gradient. *Soil Biology and Biochemistry*, **43,** 835-844.

Fellman, J.B., Hood, E., Edwards, R.T. & Jones, J.B. 2009. Uptake of allochthonous dissolved organic matter from soil and salmon in coastal temperate rainforest streams. *Ecosystems*, **12**, 747-759.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T. & Andersen, D.T. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, **46,** 38-48.

Nishimura, S., Maie, N., Baba, M., Sudo, T., Sugiura, T. & Shima, E. 2012. Changes in the quality of chromophoric dissolved organic matter leached from senescent leaf litter during the early decomposition. *Journal of Environmental Quality*, **41**, 823-833.

Santín, C., Yamashita, Y., Otero, X.L., Álvarez, M.Á. & Jaffé, R. 2009. Characterizing humic substances from estuarine soils and sediments by excitation-emission matrix spectroscopy and parallel factor analysis. *Biogeochemistry*, **96**, 131-147.

van Hees, P.A.W., Jones, D.L., Finlay, R., Godbold, D.L. & Lundström, U.S. 2005. The carbon we do not see - the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: a review. *Soil Biology and Biochemistry*, **37**, 1-13.

Wang, T.M., Wang, Y.Y., Xiang, B. & Hu, Y. 2011. Effect freezing and thawing cycles on fluorescence characterization of black soil dissolved organic matter. *Spectroscopy and Spectral Analysis*, **31**, 2136-2140.